Platinum(II) *N*-heterocyclic carbene complexes: coordination and cyclometallation.

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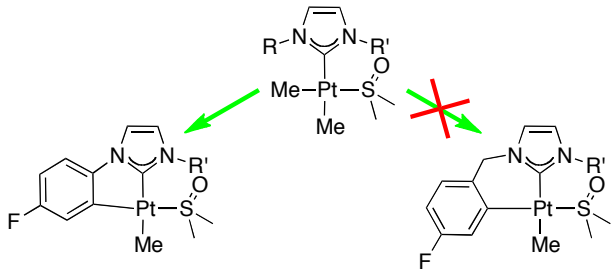
Abstract



Four different NHC ligands have been coordinated to Pt(II) centres; for the first time cyclometallation of the NHC ligand was observed, but only when the platinum centre had a DMSO and two methyl co-ligands. Cyclometallation resulted in the exclusive formation of five-membered rings, and the absence of any double cyclometallation reactions with appropriate ligands rules out the possibility of an oxidative addition type mechanism for the cyclometallation reaction.

Introduction

In the past ten years the nitrogen stabilised heterocyclic carbene (NHC) ligand has progressed from being an academic curiosity to its present ubiquity: it is now considered as a versatile ligand that is often used in preference to the more traditional phosphine.[1] Electronically, the NHC ligand has often been considered to be a better σ donor, and a weaker π acceptor, than the phosphine ligand,[2] though contrary evidence regarding their π acceptor ability is available.[3] Relatively simple synthetic procedures leading to precursor imidazolium salts have been elucidated,[4] and many routes that allow the introduction of an NHC ligand to a metal centre have been developed. The reaction of imidazolium salts with silver oxide giving an NHC complex of silver, which serves as a useful trans-metallating reagent, has proved particularly popular,[5-8] and we use it in this paper. Other interesting methods include the utilisation of an electron-reservoir complex, together with air, to generate NHCs,[9] or the use

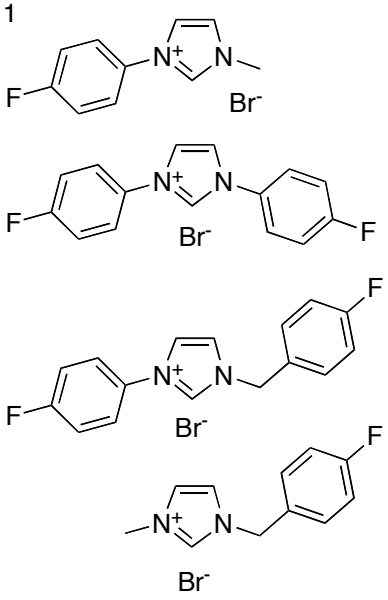
of imidazolium-2-carboxylates which lose CO_2 to generate NHCs,[10] though, increasingly, direct reaction of the imidazolium salt with the metal has found favour.[11-14] More recently, NHC ligands have been shown not to be innocent spectators, but reactive intermediates themselves, with a number of new products being formed.[15, 16]

Whilst most the studies on catalytically active systems have their emphasis on palladium based chemistry,[17] platinum complexes are also of interest. Amongst other uses, platinum complexes with NHC ligands have been used for the reductive cyclization of diynes and enynes[18], the catalytic diboration of unsaturated molecules[19] and the tandem hydroboration-cross coupling reaction.[20] Thus the clean, high yielding synthesis of NHC platinum complexes is of considerable current interest. Cyclometallation[21] of NHC ligands has been reported many times, but to the best of our knowledge none of these examples are cycloplatinated complexes. By contrast, a search of the Cambridge Crystallographic Database[22] reveals fifty-eight structurally characterised cyclopalladated NHC complexes; it is of relevance to note that none of these complexes have a three or four membered cyclometallated ring, only six[23, 24] have a five membered ring, forty-two have a six membered ring, twelve a seven membered ring and eight an eight membered ring.

Results and Discussion

In order to establish some of the principles behind the cycloplatination of NHC ligands, we studied the reactivity of four different imidazolium salts **1** with platinum sources, Scheme 1.

Scheme 1



1a: R = 4-F-phenyl, R' = Me

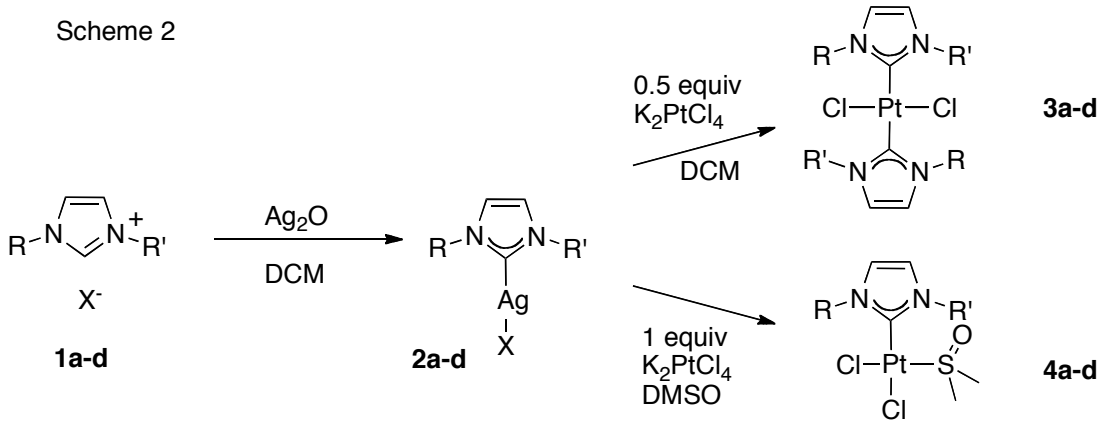
1b: R = R' = 4-F-phenyl

1c: R = 4-F-phenyl, R' = 4-F-benzyl

1d: R = Me, R' = 4-F-benzyl

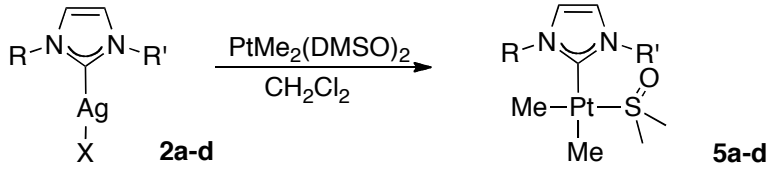
Using our previously described methodology,[25] we can selectively introduce either one or two NHC ligands at a platinum centre, via silver complexes, Scheme 2.

Scheme 2



We had hoped that we could induce one or both of the complexes **3** or **4** to undergo a cyclometallation reaction, but we were unable to find suitable conditions and reagents to facilitate such transformations. The reagent $PtMe_2(DMSO)_2$ has been reported[26] to induce facile cyclometallation reactions and we thus tried it. Reaction of the silver NHC complexes **2** with $PtMe_2(DMSO)_2$ has not previously been documented, but we can report that it works well as another method of selectively introducing a single NHC ligand to a platinum(II) centre, giving excellent yields, Scheme 3.

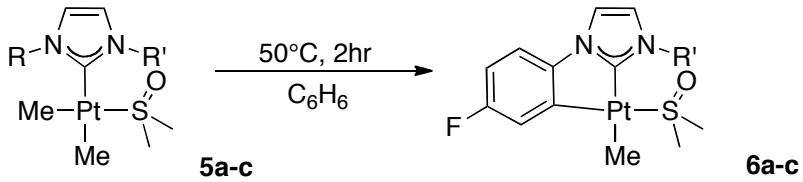
Scheme 3



A *cis* orientation of the two methyl groups in complexes **5** can clearly be established from the ^{1}H NMR as two signals (relative integral three) are seen for these groups. Different couplings from these protons to the central platinum are also seen: the $^2J_{Pt\text{-}H}$ for the methyl *trans* to the NHC is typically 60 Hz, whereas that of the methyl *trans* to the DMSO is typically 80 Hz; such differences are readily accounted for by the differing *trans* influences of the NHC and DMSO ligands. In the complexes with unsymmetrical NHC ligands (i.e. R ≠ R') two signals (each of relative integral three) are seen for the DMSO protons at room temperature, consistent with the plane of the NHC ligand being perpendicular to the coordination plane of the platinum, together with restricted rotation about the NHC–Pt bond.[25, 27]

Gentle heating of the new complexes **5a-c** results in a C-H activation reaction of the phenyl ring, similar to that seen before.[26, 28, 29] Cyclometallated products **6a-c** are now seen, presumably accompanied by the elimination of methane, Scheme 4.

Scheme 4



The new complexes **6a-c** are easily identified by NMR spectroscopy. In the ^{1}H NMR only one Me group bonded directly to platinum is observed, all six protons of the DMSO become equivalent and the coupling pattern of the protons on the phenyl group change (from two sets of two protons, to three individual resonances; one with Pt satellites). The ^{19}F NMR shows a signal for a fluorine with platinum satellites, consistent with a cyclometallation.

The platinum bound methyl groups in **6a-c** are confirmed to be *trans* to the NHC ligand via a series of NOE experiments; if we take the R' = Me complex **6a** as a representative example, we can see NOE interactions between the Pt-Me and the cyclometallated ring, between the Pt-Me and the DMSO protons and between the DMSO protons and the R' group (and *vice versa*, in each case). Within the coordination sphere of the platinum in **6** this geometry is the one we would expect as it is the arrangement without the aryl and alkyl carbon donors being *trans* to each other; similar to other work,[30] it puts the alkyl carbon donor *trans* to the NHC ligand. The cyclometallation reaction brings the plane of the NHC ring into alignment with that of the coordination plane of the platinum and renders the all protons of the DMSO co-ligand equivalent. Relatively small couplings (typically 15 Hz) from the platinum to the DMSO protons are observed in both complexes **5** and **6**, consistent the DMSO being *trans* to a high *trans*-influence ligand in both complexes. However, relatively large (around 70 Hz) three bond couplings from the central platinum to the protons *ortho* to both the Pt and the F in cyclometallated ring are seen in complexes **6**. Previously we have seen couplings in the range of 24-55 Hz[31-34] for this type of proton, with coupling this large only when the cyclometallated ring is *trans* to an agostic interaction.[35] The coupling of the platinum to the fluorine is also larger than normal,[34] again similar to that seen in agostic complex.[35]

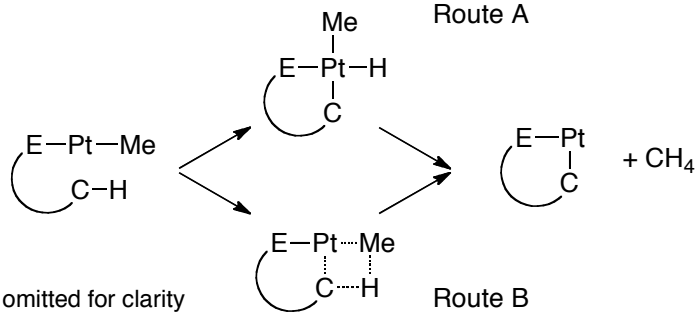
In principle the single cyclometallation of complex **5c** could have taken place in one of two ways: either the phenyl ring or the benzyl ring attached to the NHC could have been activated; the possibility also exists for a double cyclometallation. In practice only one cyclometallated product was ever observed, even upon prolonged heating. This single product was confirmed to be the one in which only the phenyl ring was cyclometallated via a series of NOE experiments: the clearly distinct benzyl and DMSO protons were shown to be close to each other and, crucially, both showed enhancements upon irradiation of the signals for the non-cyclometallated ring (and vice versa) with no enhancements observed between these

signals and the cyclometallated ring. The absence of any product containing a cyclometallated benzyl group is consistent with the observation of no reaction at all when complex **5d** was heated in benzene, even when that heating was maintained for a week.

Clearly, therefore this methodology gives rise to a preference for cyclometallation of a phenyl ring (to give a five-membered metallacycle) over the cyclometallation of a benzyl group (to give a six-membered metallacycle); it should be noted that both metallation reactions involve the activation of an sp^2 hybridised C-H bond. Such an outcome is very much in line with historical precedent: five-membered metallacycles account for the majority of published examples.[36, 37] However, given that structurally characterised six-membered NHC-palladacycles outnumber five-membered NHC-palladacycles forty-two to six, we can assume there would be nothing inherently unstable about a six membered NHC-platinacycle, and the reason we do not observe them is in someway related to the kinetics of the pathway leading to our products. Extended heating of compounds **6b** or **6c** did not result in any double cyclometallation. Given the observations above, regarding complex **5d**, the lack of any subsequent reaction with **6c** is perhaps not surprising. The second cyclometallation of compound **6b** would, however, lead to a second five membered ring and, by analogy with pyridine[31, 32, 38] and phosphine[39] systems, ought to be accessible. Once again, it is presumably the reaction pathway that inhibits the reaction, rather than the inherent stability of the product.

There are two widely accepted extremes of mechanisms for C-H activation reactions of this type: an oxidative addition type mechanism, route A, Scheme 5 and an "electrophilic" mechanism that has many similarities to σ-bond metathesis, route B, Scheme 5.[40] Evidence for both types of process has been presented for platinum(II).[41-43]

Scheme 5



Other ligands on Pt omitted for clarity

It is worth considering one[42] of these reports in more detail as it deals with the cycloplatination of a complex rather similar to ours: an *o*-tolylphosphine is coordinated to a dimethyl platinum centre that also has a DMSO ligand. Strong evidence is presented that the DMSO ligand dissociates prior to oxidative addition of the sp^3 C-H bond of the phosphine, giving a methyl hydride which then eliminates methane with the concomitant recoordination of the DMSO. However, if such a process operated in our reactions, it would be hard to see

why the cyclometallation of **5d** did not take place, or why complex **6b** did not undergo a second cyclometallation. Conversely, if we were to expect the cyclometallation of the second phenyl ring of **6b** to go via the electrophilic route, with some sort of concerted coupling of the hydrogen with the methyl group, it would be imperative that the methyl group be adjacent to the phenyl ring. Since it is not we can easily understand a lack of reactivity if this route were operational.

The lack of any cyclometallation of the benzyl groups is harder to understand, but there ought to be no reason why an oxidative addition type reaction could not take place: the six membered ring formed ought to be perfectly stable; a concerted process would require the formation of a slightly bigger ring in the transition state, and perhaps that is unfavourable.

Whilst we have not undertaken an exhaustive study of our reaction, it seems likely, therefore, that our cycloplatinations do go via a mechanism that is closer to the electrophilic route than it is to the oxidative addition route. Whether the difference between our chemistry and that of the example noted above[42] is due to the nature of the C-H bond being activated (in our case an sp^2 hybridised carbon, in theirs an sp^3) or a function of the ligand (in our case an NHC, in their case a phosphine) is currently unclear, and we propose to investigate the matter further.

Conclusions

Four different NHC ligands have been coordinated to Pt(II) centres. Three of the four ligands underwent cyclometallation reactions but only when the platinum centre had a DMSO and two methyl co-ligands. These products represent the first reported examples of cycloplatinated NHC ligands an our reaction conditions resulted in the exclusive formation of five-membered metallacycles. The absence of any double cyclometallation reactions with appropriate ligands rules out the possibility of an oxidative addition type mechanism for the cyclometallation reaction.

Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400, 500 or 600 in $CDCl_3$, CD_2Cl_2 or C_6D_6; ^1H and ^{19}F spectra were observed directly and are referenced to external TMS or $CFCl_3$, respectively. ^{195}Pt chemical shifts quoted are taken from 2D ^1H-^{195}Pt HETCOR spectra and are referenced to external Na_2PtCl_6. Elemental analyses were performed by Warwick Analytical Services.

Imidazolium salts were synthesised via literature routes: **1a** via the copper catalysed coupling of 4-fluoro-phenyl boronic acid with imidazole,[44] followed by reaction with MeI; **1b** via the condensation of 4-fluoro-aniline with glyoxal,[45] followed by reaction with chloromethylethyl

ether; **1c** via the copper catalysed coupling of 4-fluoro-phenyl boronic acid with imidazole, followed by reaction with 4-fluoro-benzyl bromide; **1d** via the reaction of methylimidazole with 4-fluoro-benzyl bromide. Silver NHC salts were then prepared via the reaction of imidazolium salt with silver oxide in DCM.[5, 6, 8]

Synthesis of the [Pt(NHC)(DMSO)(Me)$_2$] complexes (5)

Full details are given for **5a** only: analogous complexes were prepared in a similar manner. To a solution of 62 mg (0.151 mmol) of **2a** in CH_2Cl_2 (20 ml), was added 57.5 mg (0.151 mmol) of [Pt(Me)$_2$DMSO$_2$]. The mixture was stirred at room temperature, under nitrogen, for six hours; the colour changed quickly to a milky-white suspension. The mixture was filtered through celite to give a colourless solution, which was then concentrated to small volume and treated with petrol ether to give a white precipitate, which was collected the give analytically pure material. Yield 79%.

5a Anal. Calcd. for $C_{14}H_{21}FN_2OPtS$: C, 35.07%, H, 4.41%, N, 5.84%. found: C, 34.74%, H, 4.45%, N, 5.65%.

NMR (C_6D_6) δ_H: 7.6 (2H, dd, J = 8.8, J_{F-H}= 4.8 Hz, H_o), 6.68 (2H, t, J = J_{F-H}= 8.6 Hz, H_m), 6.26 (1H, d, J = 2, J_{Pt-H} = 6.6 Hz, H_{imid}), 5.96 (d, 1H, J = 2, J_{Pt-H}= 7 Hz, H_{imid}), 3.41 (3H, s, Me_{NHC}), 2.45 (3H, s, J_{Pt-H}= 15 Hz, DMSO), 2.05 (3H, s, J_{Pt-H}= 15 Hz, DMSO), 1.09 (3H, s, J_{Pt-H} = 81 Hz, Me), 0.56 (3H, s, J_{Pt-H} = 62 Hz, Me); δ_F: -114.06; δ_{Pt}: -3914.

5b Anal. Calcd. for $C_{19}H_{22}F_2N_2OPtS$: C, 40.78%, H, 3.96%, N, 5.01%. Found: C, 40.21%, H, 4.21%, N, 4.82%.

NMR (C_6D_6) δ_H: 7.98 (2H, dd, J = 8.9, J_{H-F} = 5 Hz, H_o), 7.63 (2H s, H_{imid}), 7.30 (2H, t, J = J_{F-H}= 8.7 Hz, H_m), 2.56 (6H, s, J_{Pt-H}= 15Hz, DMSO), 0.1 (3H, s, J_{Pt-H}= 82 Hz, Me), -0.24 (3H, s, J_{Pt-H}= 65 Hz, Me); δ_F: -115.54; δ_{Pt}: -3905.

5c. Anal. Calcd. per $C_{20}H_{24}F_2N_2OPtS$: C, 41.88%, H, 4.22%, N, 4.88%. found: C, 41.40%, H, 4.29%, N, 4.89%.

NMR (C_6D_6) δ_H: 7.66 (2H, dd, J = 8, J_{H-F}= 4.4 Hz, H_o), 7.07 (2H, dd, J = 8, J_{H-F}= 4.6 Hz, H_o), 6.80 (2H, t, J = J_{F-H}= 8 Hz, H_m), 6.71 (2H, t, J = J_{F-H}= 8 Hz, H_m), 6.36 (1H, d, J = 2 Hz, H_{imid}), 6.12 (1H, d, J = 2 Hz, H_{imid}), 5.89 (d, 1H, J = 14 Hz, benzyl), 4.72 (1H, d, J = 14 Hz, benzyl), 2.33 (3H, s, J_{Pt-H}= 14 Hz, DMSO), 2.03 (3H, s, J_{Pt-H}= 15 Hz, DMSO), 1.13 (3H, s, J_{Pt-H}= 82 Hz, Me), 0.48 (3H, s, J_{Pt-H}= 64 Hz Me); δ_F: -113.80 (1F, s), -114.24 (1F, s); δ_{Pt}: -3919ppm.

5d. Anal. Calcd. for $C_{15}H_{23}FN_2OPtS$: C, 36.51%, H, 4.70%, N, 5.68%. found: C, 36.00%, H, 4.59%, N, 5.45%.

NMR (C_6D_6) δ_H: 6.94 (2H, dd, J = 8.8, J_{H-F}= 5.4 Hz, H_o), 6.73 (2H, t, J = J_{F-H}= 8.67 Hz, H_m), 5.98 (1H, d, J = 1.9 Hz, H_{imid}),), 5.92 (1H, d, J = 1.9 Hz, H_{imid}), 5.55 (d, 1H, J = 15 Hz, benzyl), 4.89 (1H, d, J = 15 Hz, benzyl), 3.39 (3H, s, Me_{NHC}), 2.51 (3H, s, J_{Pt-H}= 14.7 Hz,

DMSO), 2.38 (3H, s, J_{Pt-H}= 14.8 Hz, DMSO), 1.14 (3H, s, J_{Pt-H}= 81 Hz, Me), 0.67 (3H, s, J_{Pt-H}= 63 Hz Me); δ_F: -115.04; δ_{Pt}: -4002ppm.

Synthesis of the [Pt(NHC-H)(DMSO)Me] complexes (6)

Full details are given for **6a** only: analogous complexes were prepared in a similar manner. A solution of 42 mg of [Pt(NHC)DMSOMe$_2$], **5a**, was heated (50°C, 2hr), with stirring, in freshly distilled benzene. During this time the colour of the solution changed from colourless to yellow. Then the solution was concentrated to small volume and treated with pet ether (40-60) to precipitate the product. The solid was then filtered off to give an analytically pure product as a yellow solid. Yield 69%.

6a. Anal. Calcd. for $C_{13}H_{17}FN_2OPtS$: C, 33.69%, H, 3.70%, N, 6.04%. found: C, 33.77%, H, 3.44%, N, 6.11%.

NMR (C_6D_6) δ_H: 8.07 (1H, dd, J_{H-F}= 10.2, J= 2.4, J_{Pt-H}= 71 Hz, H_o), 6.65 (1H, td, J_{H-F} = J = 8.2, J = 2.5 Hz, H_m), 6.43 (1H, dd, J = 8.6, J_{H-F} = 5.0 Hz, H_o), 6.27 (1H, s, H_{imid}), 5.65 (1H, s, H_{imid}), 3.57 (3H, s, Me_{NHC}), 2.45 (6H, s, J_{Pt-H}= 16 Hz, DMSO), 0.63 (3H, s, J_{Pt-H}= 64 Hz, Pt-Me); δ_F: -118.5 (s, J_{Pt-F} = 57 Hz); δ_{Pt}: -4210ppm.

6b. Yield 74%. Anal. Calcd. for $C_{18}H_{18}F_2N_2OPtS$: C, 39.78%, H, 3.34%, N, 5.15%. found: C, 40.12%, H, 3.43%, N, 4.95%.

NMR (D_6-acetone) δ_H: 7.95 (1H, d, J = 2 Hz, H_{imid}), 7.67 (2H, dd, J_{H-F}= 8.8, J = 4.7 Hz), 7.52 (1H, d, J = 2 Hz, H_{imid}), 7.45 (1H, dd, J_{H-F} = 8.6, J = 4.5 Hz), 7.42 (1H, dd, J_{H-F}= 8.2, J = 2.0, J_{Pt-H}= 65 Hz), 7.31 (2H, t, J = J_{H-F}= 8 Hz), 6.83 (1H, td, J = J_{H-F} = 8.5, J = 1.8 Hz), 2.86 (6H, s, J_{Pt-H}= 16 Hz, DMSO), 0.45(s, 3H, J_{Pt-H}= 64 Hz Me); δ_F: -115.49 (1F, s), -120.01 (1F, s, J_{Pt-F} = 55 Hz); δ_{Pt}: -4152ppm.

6c. Anal. Calcd. for $C_{19}H_{20}F_2N_2OPtS$: C, 40.93%, H, 3.62%, N, 5.02%. found: C, 40.68%, H, 3.61%, N, 5.32%.

NMR (C_6D_6) δ_H: 8.10 (1H, dd, J = 3, J_{H-F}= 10, J_{Pt-H}= 70 Hz, H_o), 7.50 (2H, dd, J = 8, J_{H-F}= 4.6 Hz), 7.20 (1H, dd, J = 9, J_{H-F}= 5 Hz), 6.75 (1H, td, J = J_{F-H}= 9, J = 3 Hz, H_p), 6.68 (2H, t, J = J_{F-H}= 8 Hz, H_m), 6.24 (1H, d, J = 2 Hz, H_{imid}), 6.05 (1H, d, J = 2 Hz, H_{imid}), 5.70 (s, 2H, benzyl), 2.48 (6H, s, J_{Pt-H}= 13 Hz, DMSO), 1.25 (3H, s, J_{Pt-H}= 72 Hz Me); δ_F: -114.80 (1F, s), -117.56 (1F, s, J_{Pt-F} = 56 Hz); δ_{Pt}: -4196ppm.

References

1. R. H. Crabtree, *J. Organomet. Chem.,* 2005**, 690**, 5451-5457.
2. W. A. Herrmann, J. Schutz, G. D. Frey and E. Herdtweck, *Organometallics,* 2006**, 25**, 2437-2448.

3. L. Cavallo, A. Correa, C. Costabile and H. Jacobsen, *J. Organomet. Chem.,* 2005**, 690**, 5407-5413.
4. M. R. Grimmett, *Imidazole and Benzimidazole Synthesis*. Academic Press: London, 1997.
5. H. M. J. Wang and I. J. B. Lin, *Organometallics,* 1998**, 17**, 972-975.
6. I. J. B. Lin and C. S. Vasam, *Comments Inorg. Chem.,* 2004**, 25**, 75-129.
7. I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.,* 2007**, 251**, 642-670.
8. C. P. Newman, G. J. Clarkson and J. P. Rourke, *J. Organomet. Chem.,* 2007, 4962-4968.
9. D. Méry, J. R. Aranzaes and D. Astruc, *J. Am. Chem. Soc.,* 2006**, 128**, 5602-5603.
10. A. M. Voutchkova, L. N. Appelhans, A. R. Chianese and R. H. Crabtree, *J. Am. Chem. Soc.,* 2005**, 127**, 17624-17625.
11. D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.,* 2001**, 123**, 8317-8328.
12. D. S. McGuinness, K. J. Cavell and B. F. Yates, *Chem. Commun.,* 2001, 355-356.
13. A. A. Danopoulos, S. Winston and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* 2002, 3090-3091.
14. M. Viciano, M. Poyatos, M. Sanaú, E. Peris, A. Rossin, G. Ujaque and A. Lledós, *Organometallics,* 2006**, 25**, 1120-1134.
15. C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.,* 2004**, 248**, 2247-2273.
16. K. Randell, M. J. Stanford, G. J. Clarkson and J. P. Rourke, *J. Organomet. Chem.,* 2006**, 691**, 3411-3415.
17. E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.,* 2007**, 46**, 2768-2813.
18. I. G. Jung, J. Seo, S. I. Lee, S. Y. Choi and Y. K. Chung, *Organometallics,* 2006**, 25**, 4240-4242.
19. V. Lillo, J. Mata, J. Ramirez, E. Peris and E. Fernandez, *Organometallics,* 2006**, 25**, 5829-5831.
20. V. Lillo, J. A. Mata, A. M. Segarra, E. Peris and E. Fernandez, *Chem. Commun.,* 2007, 2184-2186.
21. M. Albrecht, *Chem. Rev.,* 2009**, 110**, 576-623.
22. D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.,* 1996**, 36**, 746-749.
23. N. Stylianides, A. A. Danopoulos, D. Pugh, F. Hancock and A. Zanotti-Gerosa, *Organometallics,* 2007**, 26**, 5627-5635.
24. Z. Liu, T. Zhang and M. Shi, *Organometallics,* 2008**, 27**, 2668-2671.
25. C. P. Newman, R. J. Deeth, G. J. Clarkson and J. P. Rourke, *Organometallics,* 2007**, 26**, 6225-6233.
26. A. Zucca, A. Doppiu, M. A. Cinellu, S. Stoccoro, G. Minghetti and M. Manassero, *Organometallics,* 2002**, 21**, 783-785.
27. J. Mamtora, S. H. Crosby, C. P. Newman, G. J. Clarkson and J. P. Rourke, *Organometallics,* 2008**, 29**, 5559-5565.
28. G. Minghetti, S. Stoccoro, M. A. Cinellu, B. Soro and A. Zucca, *Organometallics,* 2003**, 22**, 4770-4777.
29. A. Zucca, G. L. Petretto, S. Stoccoro, M. A. Cinellu, M. Manassero, C. Manassero and G. Minghetti, *Organometallics,* 2009**, 28**, 2150-2159.
30. S. K. Yen, D. J. Young, H. V. Huynh, L. L. Koh and T. S. A. Hor, *Chem. Commun.,* 2009, 6831-6833.
31. G. W. V. Cave, N. W. Alcock and J. P. Rourke, *Organometallics,* 1999**, 18**, 1801-1803.
32. G. W. V. Cave, F. P. Fanizzi, R. J. Deeth, W. Errington and J. P. Rourke, *Organometallics,* 2000**, 19**, 1355-1364.

33. C. P. Newman, G. W. V. Cave, M. Wong, W. Errington, N. W. Alcock and J. P. Rourke, *J. Chem. Soc., Dalton Trans.,* 2001, 2678-2682.
34. C. P. Newman, K. Casey-Green, G. J. Clarkson, G. W. V. Cave, W. Errington and J. P. Rourke, *Dalton Trans.,* 2007, 3170-3182.
35. S. H. Crosby, G. J. Clarkson and J. P. Rourke, *J. Am. Chem. Soc.,* 2009**, 131**, 14142-14143.
36. M. Bruce, *Angew. Chem., Int. Ed. Engl.,* 1977**, 16**, 73.
37. I. Omae, *Coord. Chem. Rev.,* 2004**, 248**, 995-1023.
38. L. Chassot, E. Muller and A. von Zelewsky, *Inorg. Chem.,* 1984**, 23**, 4249-4253.
39. A. J. Cheney, W. S. McDonald, K. O'Flynn, B. L. Shaw and B. L. Turtle, *J. Chem. Soc., Chem. Commun.,* 1973, 128-129.
40. M. Lersch and M. Tilset, *Chem. Rev.,* 2005**, 105**, 2471-2526.
41. S. Otto, A. Chanda, P. V. Samuleev and A. D. Ryabov, *Eur. J. Inorg. Chem.,* 2006, 2561-2565.
42. R. Romeo, M. R. Plutino and A. Romeo, *Helv. Chim. Acta,* 2005**, 88**, 507-522.
43. A. Marrone, N. Re and R. Romeo, *Organometallics,* 2008**, 27**, 2215-2222.
44. J. B. Lan, L. Chen, X. Q. Yu, J. S. You and R. G. Xie, *Chem. Commun.,* 2004, 188-189.
45. A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron,* 1999**, 55**, 14523-14534.